

**P-N HETEROJUNCTION STRUCTURE OF ZINC OXIDE-BASED
NANOROD AND SEMICONDUCTOR THIN FILM, PREPARATION
THEREOF, AND NANO-DEVICE COMPRISING SAME**

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Field of the Invention

The present invention relates to a novel heterojunction structure comprising a p-type semiconductor thin film and an n-type ZnO-based
10 nanorod epitaxially grown thereon, which provides a light emitting device having improved luminescence properties.

Background of the Invention

15 The Gallium nitride (GaN)-based blue light emitting diode (LED) developed by Nichia Chemical Co., Ltd. in 1993 uses a GaN p-n thin film junction to provide blue and green LED devices, and in 1997, a short wavelength (404 nm) blue LED having a life span of about 10,000 hours at room temperature has been developed using a nitride semiconductor.

20 Recently, an n-type oxide semiconductor, zinc oxide (ZnO), has attracted attention as an another efficient light emitting ($\lambda = 380$ nm) material at room temperature due to its interesting features: (1) a direct transition band structure, (2) a low power threshold for optical pumping at room temperature and (3) a large exciton binding energy (60 meV).

25 However, the development of a p-n heterojunction structure of zinc oxide has been hampered due to the difficulty of fabricating p-type ZnO.

Summary of the Invention

Accordingly, it is a primary object of the present invention to provide a novel heterojunction structure formed by way of using n-ZnO in the form of a nanorod and a p-type semiconductor material other than p-ZnO in the form of a thin film, which can be advantageously used for nano-devices such as LED, field effect transistor, photodetector, sensor, etc.

It is another object of the present invention to provide a method for preparing such a structure.

It is a further object of the present invention to provide a nano-device or an array thereof comprising such a structure.

In accordance with one aspect of the present invention, there is provided a heterojunction structure comprising a p-type semiconductor thin film and an n-type ZnO-based nanorod epitaxially grown thereon.

In accordance with another aspect of the present invention, there is provided a method for preparing said heterojunction structure, which comprises bringing the vapors of a Zn-containing metal organic compound and an O₂-containing compound as reactants separately into contact with a p-type semiconductor thin film at a temperature in the range of 400 to 700 °C under a pressure in the range of 0.1 to 10 torr to form a ZnO nanorod on the surface of the semiconductor film.

In accordance with a still another aspect of the present invention, there is provided a nano-device or an array thereof comprising said heterojunction structure.

Brief Description of the Drawings

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The above and other objects and features of the present invention will become apparent from the following description of the invention, when taken

in conjunction with the accompanying drawings, which respectively show:

Fig. 1: a schematic diagram of the process for preparing a p-n heterojunction structure in accordance with Example 1 of the present invention;

5 Fig. 2: a schematic diagram of the light emitting diode device comprising a p-n heterojunction structure in accordance with the present invention;

Figs. 3(a) and 3(b): scanning electron microscope scans of the ZnO-based p-n heterojunction structures obtained in Examples 1 and 2 of the present invention, respectively; and

10 Fig. 4: the light emission spectrum of the LED obtained in Example 2 of the present invention, which comprises the heterojunction structure formed by epitaxially growing n-type ZnO nanorods on a p-type GaN thin film.

15 Detailed Description of the Invention

The inventive heterojunction structure characteristically comprises a p-type semiconductor thin film and an n-type ZnO-based nanorod epitaxially grown thereon.

20 Also, a nano-device comprising said heterojunction structure can be fabricated by forming electrodes using a thermal or electron beam evaporation technique on the opposing surfaces of the p-type semiconductor thin film and n-type nanorods of the heterojunction structure.

25 In the inventive heterojunction structure, the p-type semiconductor thin film may be in the form of a single crystal, or a thin film formed on a substrate using a conventional metal organic chemical vapor deposition

(MOCVD) method which comprises heating a substrate and bringing the vapors of appropriate precursors into contact with the surface of the substrate.

The p-type semiconductor thin film of the inventive structure may have a thickness ranging from 50 nm to 200 μm .

5 Suitable for use as the p-type semiconductor for a thin film is a material having a band-gap of 1.5 to 4.5 eV, and representative examples thereof include a III-VB group semiconductor such as GaN, AlN, GaP, GaAs, etc.; a II-VIB group semiconductor such as ZnSe, CdSe, CdS, ZnS, etc.; and a semiconductor such as SrCu_2O_2 , SiC, Si, etc.

10 Further, the ZnO-based nanorod grown on the p-type semiconductor thin film may be a ZnO nanorod, or a ZnO nanorod doped or coated with a heteromaterial. Exemplary heteromaterial dopants include Mg, Mn, Cd, Se, etc.; and doped heteromaterials, $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ ($0 < x < 1$), $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($0 < x < 1$), $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ ($0 < x < 1$), $\text{Zn}_{1-x}\text{Se}_x\text{O}$ ($0 < x < 1$) and the like.

15 The inventive heterojunction structure can be prepared by epitaxially growing ZnO-based nanorods onto a p-type semiconductor thin film using a metal organic chemical vapor deposition (MOCVD) method, which comprises brining the vapors of a Zn-containing metal organic compound and an O_2 -containing compound as reactants separately into contact with a p-type
20 semiconductor thin film at 400 to 700 $^\circ\text{C}$ under a pressure in the range of 0.1 to 10 torr.

 If necessary, a ZnO nanorod formed on a p-type semiconductor thin film may be doped or coated with a heteromaterial by introducing the vapor of a compound containing a heteromaterial such as Mg, Mn, Cd, Se, etc., at
25 the time of introducing the reactant vapors or after the formation of the ZnO nanorod, to form a heteromaterial-doped or coated ZnO nanorod.

 The diameter, length and density of ZnO-based nanorods formed on a

p-type semiconductor thin film can be varied depending on the reaction conditions such as the amount of gaseous reactants introduced into a reaction chamber, deposition temperature and pressure, etc., during their growth.

The nanorod on a thin film of the inventive structure may have a
 5 diameter in the range of 5 to 100 nm and a length in the range of 5 nm to 100 μm .

Exemplary Zn-containing metal organic compounds that can be used as precursors for zinc oxide in the present invention include dimethylzinc $[\text{Zn}(\text{CH}_3)_2]$, diethylzinc $[\text{Zn}(\text{C}_2\text{H}_5)_2]$, zinc acetate $[\text{Zn}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}]$,
 10 zinc acetate anhydride $[\text{Zn}(\text{OOCCH}_3)_2]$, zinc acetyl acetonate $[\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2]$, etc; O_2 -containing compound, O_2 , O_3 , NO_2 , H_2O (vapor), CO_2 , $\text{C}_4\text{H}_8\text{O}$, etc.

Further, exemplary Mg-containing metal organic compounds that can be used as precursors for nanorod doping or coating in the present invention include bis(cyclopentadienyl) magnesium $[(\text{C}_5\text{H}_5)_2\text{Mg}]$,
 15 bis(methylcyclopentadienyl) magnesium $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Mg}]$,
 bis(ethylcyclopentadienyl) magnesium $[(\text{C}_2\text{H}_5\text{C}_5\text{H}_4)_2\text{Mg}]$,
 bis(pentamethylcyclopentadienyl) magnesium $[(\text{CH}_3)_5\text{C}_5\text{H}_4)_2\text{Mg}]$, magnesium acetate $[\text{Mg}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}]$, magnesium acetate anhydride $[\text{Mg}(\text{OOCCH}_3)_2]$, magnesium acetyl acetonate $[\text{Mg}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot \text{H}_2\text{O}]$, etc;
 20 Mn-containing metal organic compound, bis(cyclopentadienyl) manganese $[(\text{C}_5\text{H}_5)_2\text{Mn}]$, etc; Cd-containing metal organic compound, diethylcadmium $[(\text{C}_2\text{H}_5)_2\text{Cd}]$, etc; Se-containing metal organic compound, diethylselenium $[(\text{C}_2\text{H}_5)_2\text{Se}]$, etc.

The inventive heterojunction structure composed of a p-type
 25 semiconductor thin film and n-type ZnO-based nanorods vertically grown thereon can be used for an LED device as shown in Fig. 2.

The heterojunction structure according to the present invention uses

ZnO having high exciton binding energy which can be advantageously used for LED having improved emission characteristics resulting from the recombination of excitons at room temperature.

Further, the inventive heterojunction structure may be a p-n nano
5 junction which facilitates electron tunneling to increase the light emission area and comprises a nanorod having a high aspect ratio, and thus it can be used for light emitting devices having high luminescence efficiency at room temperature or higher.

As ZnO-based nanorods are formed epitaxially on a thin film in the
10 inventive heterojunction structure, an array of light emitting device comprising such a structure can be easily assembled to fabricate various nanosystems.

The following Examples are intended to illustrate the present invention more specifically, without limiting the scope of the invention.

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Example 1: the growth of ZnO nanorods on a p-type GaN thin film

ZnO-based p-n heterojunction structure was prepared by the process as shown in Fig. 1 as follows.

20 An Mg-doped GaN thin film was deposited on an Al₂O₃ substrate using a conventional MOCVD technique and annealed, to obtain a p-type GaN thin film having a thickness of 2 μ m. The metal organic precursors used were trimethylgallium (TMGa) and bis(cyclopentadienyl) magnesium ((C₅H₅)₂Mg); and the nitrogen precursor, NH₃.

25 Then, n-type ZnO nanorods were vertically grown on the p-type GaN thin film thus obtained, by injecting gaseous Zn(C₂H₅)₂ and O₂ at flow rates in the ranges of 1 to 10 sccm and 20 to 100 sccm, respectively, with an argon

(Ar) carrier gas and reacting the vapors for about 1 hour, to obtain a p-n heterojunction structure comprising n-ZnO nanorods grown on the p-GaN thin film. The reactor pressure and temperature were maintained in the ranges of 0.1 to 10 torr and 400 to 700 °C, respectively, during the ZnO nanorod growth.

A scanning electron microscope (SEM) photograph of the p-n heterojunction structure thus obtained is shown in Fig. 3(a), which reveal ZnO nanorods having a 40 nm diameter and 1 μm length are uniformly and vertically grown on the surface of the GaN thin film. Further, an X-ray diffraction (XRD) study showed that the nanorods are epitaxially grown in the (0001) orientation on the GaN thin film substrate having the same orientation.

Example 2: fabrication of a light emitting diode

A light emitting diode was fabricated using the heterojunction structure prepared in Example 1 as follows.

First, the free space around the ZnO nanorods grown on a GaN thin film was filled up by depositing an insulating material (e.g., photoresist, polyimide, etc.) thereon, and then, the tip portion of the nanorods was exposed by etching using a plasma. Subsequently, a Ti (10 nm)/ Au (50 nm) top ohmic electrode was formed at the tip portion of the etched n-type nanorods; and a Pt (10 nm)/Au (50 nm) bottom electrode, on the p-type GaN thin film, by a thermal or electron beam evaporation technique. The applied accelerating voltage and emission current were in the ranges of 4 to 20 kV and 40 to 400 mA, respectively, during the electrodes deposition, which was conducted under a reactor pressure of around 10^{-5} mmHg, while

keeping the substrate temperature at room temperature.

The cross-sectional morphology of the top electrode-formed ZnO nanorods was investigated by scanning electron microscopy (SEM) and the result is shown in Fig. 3(b).

5 Also, a light emission spectrum of the LED thus obtained is shown in Fig. 4. The light emission was strong enough to be visually recognizable and its intensity did not decrease during a long period of repeated operation (several tens of cycles). Further, as shown in Fig. 4, the device has emission peaks at around 570 nm and 470 nm.

10 The above result suggests that the inventive heterojunction structure of a p-type semiconductor thin film having epitaxially grown n-type ZnO-based nanorods has excellent light emission characteristics.

 While the embodiments of the subject invention have been described and illustrated, it is obvious that various changes and modifications can be
15 made therein without departing from the spirit of the present invention which should be limited only by the scope of the appended claims.